

Claims

10/547065

1. A CO₂ sensor comprising a pH indicator and a long-lived reference luminophore, the reference luminophore either being doped in sol-gel particles and
5 co-immobilised with the pH indicator in a porous sol-gel matrix, or being immobilised in a separate oxygen impermeable layer and the pH indicator in a sol-gel matrix being laid over the impermeable layer.
2. A CO₂ sensor as claimed in claim 1 wherein the pH indicator is selected from
10 the group consisting of pH indicators including hydroxypyrene trisulphonate (HPTS), fluorescein, rhodamine B and other fluorescent pH indicators.
3. A CO₂ sensor as claimed in claim 1 or 2 wherein the long-lived reference
15 luminophore is selected from the group consisting of a luminescent complex, in particular [Ru^{II}-tris(4,7-diphenyl-1,10-phenanthroline)]Cl₂, ruthenium-based compounds with α -diimine ligands, luminescent transition metal complexes with
20 platinum metals Ru, Os, Pt, Ir, Re or Rh as the central metal atom and with α -diimine ligands, and phosphorescent porphyrins with Pt or Pd as the central metal atom or luminescent doped crystals such as manganese-activated magnesium fluorogermanate, ruby, alexandrite and Nd-Yag.
4. A CO₂ sensor as claimed in any preceding claim wherein the porous sol-gel
25 matrix is selected from the group consisting of a methyltriethoxysilane (MTEOS) sol-gel matrix, hybrid (organic-inorganic) sol-gel matrices including ethyltriethoxysilane (ETEOS), phenyltriethoxysilane (PhTEOS), n-octyl TEOS and
methyltrimethoxysilane (MTMS), and UV-curable sol-gels, soluble ormosils, or hybrid polymer matrices.
5. A CO₂ sensor as claimed in any preceding claim wherein the luminophore is a
30 ruthenium-doped sol-gel particle, in particular [Ru^{II}-tris(4,7-diphenyl-1,10-phenanthroline)]Cl₂ -doped particles.

6. A CO₂ sensor as claimed in any preceding claim wherein the pH indicator and the long-lived reference luminophore are co-immobilised in a sol-gel matrix.

7. A combined O₂ /CO₂ sensor comprising:-

5 (a) an O₂ sensor comprising an oxygen sensitive luminescent complex immobilised in a porous sol-gel matrix, and

(b) an CO₂ sensor comprising a pH indicator and a long-lived reference luminophore, the reference luminophore either being doped in sol-gel particles and co-immobilised with the pH indicator in a porous sol-gel matrix, or being immobilised in a separate
10 oxygen impermeable layer and the pH indicator in a sol-gel matrix being laid over the impermeable layer.

8. A combined O₂ /CO₂ sensor wherein the pH indicator and the long-lived reference luminophore are co-immobilised in a porous sol-gel matrix.

15 9. A combined O₂ / CO₂ sensor as claimed in claim 8 wherein the ruthenium-complex is selected from the group consisting of an oxygen sensitive luminescent complex such as ruthenium-based compounds with α -diimine ligands and luminescent transition metal complexes with platinum metals (Ru, Os, Pt, Ir, Re or
20 Rh) as the central metal atom and with α -diimine ligands, and phosphorescent porphyrins with Pt or Pd as the central metal atom or luminescent doped crystals such as manganese-activated magnesium fluorogermanate, ruby, alexandrite and Nd-Yag.

10. A combined O₂ / CO₂ sensor as claimed in claim 8 or claim 9 wherein the
25 immobilised O₂ sensor and the immobilised CO₂ sensor are coated onto the same substrate.

11. A combined O₂ / CO₂ sensor as claimed in claim 8 to 10 wherein the two sensors are coated onto the substrate side-by-side.

30 12. A combined O₂ / CO₂ sensor as claimed in any of claims 5 to 8 wherein the substrate is selected from the group consisting of plastics materials including surface-enhanced PET, PE and PET/PE laminates, adhesive plastic labels, rigid substrate

materials including glass, Perspex/PMMA, polymer materials from which DVDs are made for example polycarbonate and other polymer materials, metal, and flexible substrate materials including acetate or flexible polymer materials, paper, optical fibre or glass/plastic capillary tubes.

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13. A method of making a CO₂ sensor comprising :-

(1) synthesis of an Ru(dpp)₃(TSPS)₂ ion-pair comprising mixing dissolved Ru(dpp)₃Cl₂ with trimethylsilylpropane sulfonic acid, sodium salt and allowing the ion-pair to precipitate,

10 (2) synthesis of the particles comprising condensing the dissolved Ru(dpp)₃(TSPS)₂ ion-pair with TEOS and halting the condensation reaction with alcohol, washing the condensate with alcohol and drying the condensate, and

(3) and fabrication of the CO₂ sensor films comprising either (a.) suspending the doped reference particles in the coimmobilisation matrix solution, mixing the
15 coimmobilisation matrix solution into a pH indicator solution which comprises a pH indicator in a quaternary ammonium hydroxide solution, and saturating the mixture immediately with CO₂ followed by deposition onto a substrate or (b.) a dual-layer configuration where a low oxygen-sensitivity ruthenium complex is sealed in an oxygen impermeable layer and over-coated with the HPTS-based CO₂ sensing layer.

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14. A method as claimed in claim 13 wherein the quaternary ammonium hydroxide is selected from the group consisting of cetyl-trimethyl ammonium hydroxide (CTA-OH), tetra-octyl ammonium hydroxide (TOA-OH) or tetra-butyl ammonium hydroxide (TBA-OH) or other quaternary ammonium hydroxides.

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15. A method as claimed in claim 13 or 14 wherein the pH indicator is selected from the group consisting pH indicators including hydroxypyrene trisulphonate (HPTS), fluorescein, rhodamine B and other fluorescent pH indicators.

30 16. A packaging medium having a combined CO₂ sensor and an O₂ sensor as claimed in any of claims 8 to 12 formed on a surface of the medium which will lie internally of the package when the package is formed.

17. A packaging medium as claimed in claim 16 wherein the sensors are formed on the packaging medium by a method selected from the group consisting of dip-coating, spin-coating, spray-coating, stamp-printing, screen-printing, ink-jet printing, pin printing, lithographic or flexographic printing or gravure printing.

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18. A quality control method comprising reading a combined O₂ / CO₂ sensor as claimed in any of claims 8 to 12, formed on the internal surface of a package, with an optical reader, and determining the levels of O₂ and CO₂ inside the package in relation to a control.

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19. A method of screen-printing a combined O₂ /CO₂ sensor as claimed in any of claims 8 to 12 onto a substrate comprising forcing the sensor sol through a mask or mesh and drying the substrate.

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20. A method of ink-jet printing a combined O₂ /CO₂ sensor as claimed in any of claims 5 to 9 onto a substrate comprising filling an ink reservoir of an ink-jet printer with sensor sol and printing the sensor sol onto the substrate using an ink-jet printer.

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21. A method of forming a gas-sensitive sensor on a substrate comprising coating or printing the substrate with a porous sol-gel matrix comprising a gas sensitive indicator.

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22. A method as claimed in claim 21 wherein the gas sensitive indicator is an oxygen-sensitive luminescent complex.

23. A method as claimed in claim 21 wherein the gas sensitive indicator is a pH indicator and a long-lived reference luminophore.

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24. A method as claimed in claim 21 wherein the gas sensitive indicator is a pH indicator and the substrate is further provided with separate oxygen impermeable layer comprising a long-lived reference luminophore.

25. A method as claimed in any of claims 21 to 23 wherein two gas sensors are formed on the substrate.

26. A method as claimed in any of claims 21 to 25 wherein the sensor is formed on the substrate by a method selected from the group consisting of dip-coating, spin-coating, spray-coating, stamp-printing, screen-printing, ink-jet printing, pin printing, lithographic or flexographic printing or gravure printing.
27. A method as claimed in any of claims 21 to 26 wherein the substrate is selected from the group consisting of plastics materials including surface-enhanced PET, PE and PET/PE laminates, adhesive plastic labels, rigid substrate materials including glass, Perspex/PMMA, polymer materials from which DVDs are made for example polycarbonate and other polymer materials, metal, and flexible substrate materials including acetate or flexible polymer materials, paper, optical fibre or glass/plastic capillary tubes.
28. A method as claimed in any of claims 21 to 27 wherein the sensor is a luminophore-based sensor.
29. A method as claimed in any of claims 21 to 27 wherein the sensor is a colorimetric-based sensor.
30. A substrate having a gas-sensitive sensor formed thereon wherein the sensor comprises a sol-gel matrix comprising a gas sensitive indicator and the sensor has been formed by printing or coating.
31. A substrate as claimed in claim 30 wherein the substrate is selected from the group consisting of plastics materials including surface-enhanced PET, PE and PET/PE laminates, adhesive plastic labels, rigid substrate materials including glass, Perspex/PMMA, polymer materials from which DVDs are made for example polycarbonate and other polymer materials, metal, and flexible substrate materials including acetate or flexible polymer materials, paper, optical fibre or glass/plastic cap.